UDC 666.76:666.1.031.2

CORROSION RESISTANCE OF GRANULAR REFRACTORIES IN MELTS OF GLASSES E AND C

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Translated from Steklo i Keramika, No. 5, pp. 23 – 25, May, 2006.

The effect of glass melts E and C used for fiber glass production on refractories with a granular structure is investigated. It is established that refractory KhS-MVU is resistant to glasses of both types.

Alumoborosilicate glasses E and C are widely used for industrial production of glass fiber in Russia and abroad [1]. The compositions of such glasses, characterized by enhanced chemical aggressiveness, are listed in Table 1. The high temperature of melting aluminoborosilicate glass and stringent requirements on the constancy of glass melt properties make it difficult to select refractory materials for glass-melting tank furnaces [2].

It is known that chromium oxide and zircon have increased resistance to such melts [3]. However, extensive application of chromium oxide refractories is limited by their high cost and complicated production technology, which involves specific molding methods, high temperatures, and a strictly controlled gaseous medium in sintering [4]. The production of zircon refractories is limited by a scarce supply of raw materials [5].

It is commonly believed that dense homogeneous materials obtained from highly disperse sintering-active powders are more resistant to aggressive melts than materials with a granular structure, as their decreased porosity and gas permeability, which is a structure-dependent property, determine their increased glass resistance. At the same time, the thermal resistance of dense materials is not as high as that of granular materials, which makes them unsuitable for those parts of glass-melting furnaces which experience abrupt temperature variations.

The purpose of our study is to investigate the interaction between glass melts E and C and refractory materials developed at the Bakor Scientific Technical Center (Table 2). These materials are produced by semi-dry molding of granular mixtures. The fillers are electromelted corundum, which is a widely used and relatively inexpensive domestic material, and sintered chromium oxide.

Static methods simulate most fully the corrosion of refractory materials in a glass-melting furnace. These methods also give a clear picture of corrosion resistance of refractories at the level of the glass melt surface, i.e., at the site of contact of three phases. One of the static methods for quality testing is the crucible method [7]. Samples for testing were molded as cylinders with a hole of diameter 22 mm and depth equal to 2/3 of the sample height. Glass E produced by the Stekloplastik JSC or glass C produced by the IRSA JSC was placed into the hole. The samples with the glasses inside were heat-treated in a muffle furnace with chromite-lantha-

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TABLE 1

Producer's country	Weight content, %								
	SiO_2	Al_2O_3	MgO	CaO	B_2O_3	R_2O	BaO	Fe_2O_3	other
				Glass E					
USA	54.8	11.5	5.0	18.0	5.5	0.8	–	–	4.4
Germany	54.4	14.6	4.5	18.0	7.5	1.0	–	–	–
France	54.2	14.4	3.7	18.3	8.5	0.7	–	0.2	–
England	53.6	14.0	0.6	21.0	10.0	0.6	0.2	–	–
Russia	53.0	15.0	4.0	17.0	10.0	0.3	–	0.1	0.6
				Glass C					
USA	65.0	4.0	3.0	14.0	5.5	8.5	–	–	–
Russia*	64.0	5.5	2.0	12.0	–	9.5	2.0	1.0	0.1

* Besides, glass C contains 2.0% ZrO_2.

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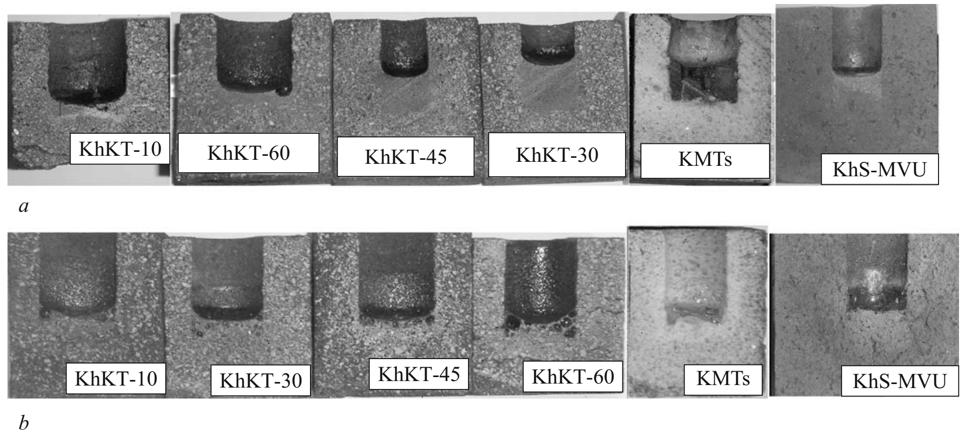

Fig. 1. Samples of refractories with glass after heat treatment: *a*) glass E (1500°C); *b*) glass C (1400°C).

num heaters at temperatures of 1500 and 1400°C, respectively, and exposed for 8 h. After testing the samples were cut parallel to the hole axis (Fig. 1).

The external inspection of refractory samples KhKT-30, 45, 60, and KhS-MVU after testing with glass E did not register any traces of corrosion under the effect of the glass melt. However, a different quantity of solidified glass in the crucibles shows that the refractories have been impregnated by the melt. It is known that the most intense corrosion is experienced by refractories at the site of contact of three phases (refractory – melt – gas). Accordingly, an increased hole diameter was registered at the glass melt level in samples KhKT-10 and KMTs.

After refractories KhKT-10, 30, 45, 60 and KhS-MVU were tested with glass C, the crucible walls showed no destruction. At the same time, refractories KhT-10, 30, 45, 60 exhibit a high propensity for bubble formation in the glass melt. The corrosive effect of the melt on refractory KMTs is manifested by an expanded diameter of the crucible hole at the glass melt level.

To clarify the destruction mechanism and study phase transformations, we performed a microscopic and petrographic analysis of samples in immersion compounds.[2]

[2] The authors express their gratitude to N. A. Popova (D. I. Mendeleev Russian Chemical Engineering University) for petrographic analysis of samples and discussion of results.

In analyzing the zone below the surface level of glass melt it was found that glass melt E penetrates the porous structure of refractories KMTs, KhKT-45, and KhKT-60. However, interaction between the refractories and the melt was not registered. Refractories KhKT-30 and KhS-MVU have a clear contact with glass; there is no impregnation or interaction with the melt; the melt is enriched with chromium oxide, which is related to the high volatility of the latter at temperatures above 1300°C [8].

Refractory KhKT-10 has a blurred contact with glass E; the melt impregnates the material via its pore structure across the whole depth of the sample. The interaction of the refractory with the glass melt occurs by mutual dissolution of the binder and the glass melt components. The solidified melt exhibits areas with crystallization nuclei, as a consequence of refractory binder components passing into the glass volume.

Glass melt C impregnates refractories KhKT-30, 45, and 60. The melt is fully crystallized in the pore structure of sample KhKT-30 with the formation of needle-shaped and rounded isometric crystals. Refractory KhKT-60 exhibits only partial crystallization, whereas in sample KhKT-45 there is no crystallization. No reaction between the melt and corundum is registered. Refractory KhS-MVU is not impregnated by glass C, however, in pores near the contact surface we observe the crystallization of glass components that are

TABLE 2

Parameter	Refractory				
	KMTs	KhKT-10-30	KhKT-45	KhKT-60	KhS-MVU
Chemical composition, wt.%:					
Al_2O_3, at least	82.5	68.0	50.0	33.0	–
ZrO_2, at least	10.0	–	–	–	–
Fe_2O_3, not more than	0.3	–	–	–	–
SiO_2	The rest	–	–	–	–
Cr_2O_3, at least	–	10.0 – 30.0	45.0	60.0	92.5
TiO_2, not more than	–	–	2.0	3.0	–
Apparent density, g/cm^3, at least	3.5	2.8	3.4	3.6	4.2
Open porosity, %, not more than	12	19	18	18	18
Compressive strength, MPa, at least	100	50	75	75	100

presumably transported by the gaseous phase. In all cases the melt is enriched with chromium oxide.

Glass melt C penetrates material KhKT-10 due to the corrosion of the binder. The binder totally passes into the melt and electromelted corundum does not dissolve in the melt.

The interaction of KMTs material with glass melt presumably proceeds as follows. Aluminum oxide from the binder reacts with silicon oxide transported by the glass melt and formed in the decomposition of zircon with the formation of mullite crystals of length 6 – 8 and thickness 1 – 2 μm. Part of the zircon dissolves in the glass and yields an “opacified glaze.” As a result, the modified zone contains 50% binder consisting of glass, mullite, zircon, and zirconium dioxide (crystallized in the monoclinic syngony). The process proceeds until the total destruction of the refractory.

The performed tests have established that refractory KhS-MVU does not get impregnated and does not react with either glass melt. Refractory KhHT-30 behaves like that only with respect to glass E. Despite the consolidation of this material due to the melt crystallizing in its pore structure, refractory KhHT-30 cannot be used for melting glass C due to its high propensity for bubble formation. Refractories KhKT-45 and KhKT-60 cannot be used for the same reason. Refractories HhKT-10 and KMTs are destroyed by glasses C and E, since the binder of these refractories contains free aluminum oxide that is not resistant to acid glass melts.

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